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THERMAL STUDIES OF METAL COMPLEXES FORMED IN Ag(I)–, Cd(II)–, UO_2(II)–, VO(II), Co(II)– AND Hg(II)–SULPHAMETHOXAZOLE SYSTEMS

H. S. Randhawa[1], *B. S. Sekhon*[1], *H. K. Sahai*[1] *and R. Lakhani*[2]

[1]Department of Chemistry, Punjab Agricultural University, Ludhiana–141004
[2]Organic Building Materials Division, Central Building Research Institute, Roorkee–247667 India

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Abstract

The mechanism of thermal decomposition of the metal complexes of sulphamethoxazole (SMZ) *viz*: [Ag(SMZ)H_2O], [Cd(SMZ)$_2$(H_2O)$_2$], [VO(SMZ)$_2$(H_2O)$_2$], [UO_2(SMZ)$_2$]·H_2O, [Hg(SMZ)$_2$(H_2O)$_2$] and [Co(SMZ)$_2$(H_2O)$_2$]·H_2O has been accomplished on the basis of TG, DTG and DTA studies. The mechanism of thermal decomposition of these complexes conforms to the stoichiometry of the complexes based on elemental analysis.

Keywords: DTA, DTG, metal complexes of SMZ, TG

Introduction

Sulphamethoxazole (SMZ) is a well known antibacterial drug and has wide applications in pharmaceutical industry. It is principally employed in the treatment of the respiratory and urinary tract infections [1]. It has already been recognized that metal complexes of ligands having biological activity are more active than free ligands [2, 3]. In view of it, the solid complexes of Ag(I), VO(II), UO_2(II), Cd(II), Co(II), Hg(II) and Ce(III) salts with SMZ have been synthesized and characterized on the basis of elemental analysis and IR and electronic spectral studies [4]. The present report deals with the thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) of SMZ and its metal complexes namely [Ag(SMZ)H_2O], [Cd(SMZ)$_2$(H_2O)$_2$], [VO(SMZ)$_2$(H_2O)$_2$], [UO_2(SMZ)$_2$]·H_2O, [Hg(SMZ)$_2$(H_2O)$_2$] and [Co(SMZ)$_2$(H_2O)$_2$]·H_2O. The aim of the thermal studies is to propose the mechanism for thermal decomposition of the complexes in order to supplement the results on the stoichiometry of the complexes based on elemental analysis [4].

Experimental

The complexes of SMZ with metal ions Ag(I), Cd(II), VO(II), UO_2(II), Co(II), Hg(II) and Ce(III) were synthesized and characterized by the methods already re-

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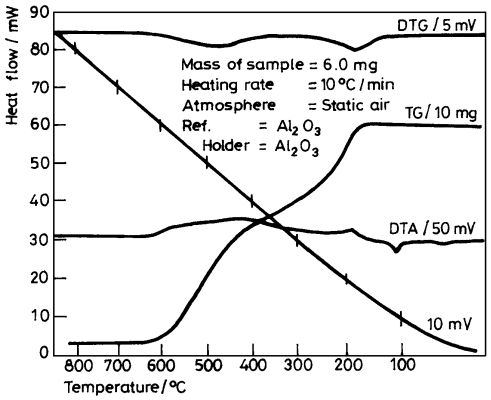

Fig. 1 TG, DTG and DTA curves of SMZ

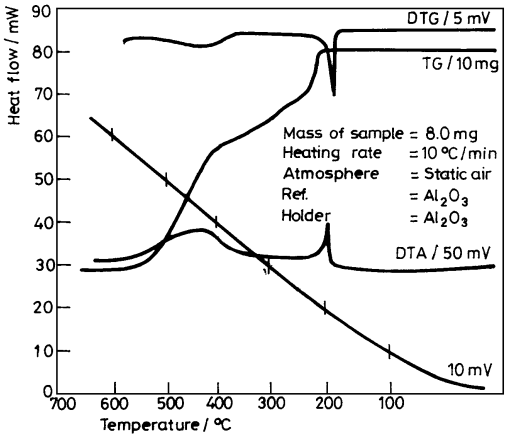

Fig. 2 TG, DTG and DTA curves of [Ag(SMZ)H_2O]

ported from our laboratory [4]. TG, DTG and DTA studies were carried out on Stanton Redcroft differential scanning calorimeter using Al_2O_3 as a standard. All the runs have been carried out at a heating rate of $10^oC\ min^{-1}$ and a chart speed of 20 cm h^{-1}. The representative curves of TG, DTG and DTA are presented in Figs 1–4.

Results and discussion

Various parameters associated with the thermal behaviour of the ligand and metal complexes *viz* Ag(I)–SMZ, Cd(II)–SMZ, VO(II)–SMZ, UO_2(II)–SMZ, Co(II)–SMZ and Hg(II)–SMZ as deduced from TG, DTG and DTA curves have been summarized in Table 1. Also recorded in Table 1 are the melting points of the complexes. The DTG and DTA curves of SMZ show that the thermal decomposition of the ligand is a two–step exothermic process. The parameters of TG curve reveal mass loss effects

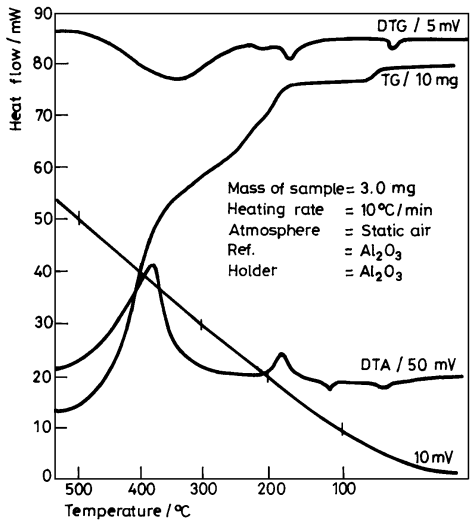

Fig. 3 TG, DTG and DTA curves of $[VO(SMZ)_2(H_2O)_2]$

in the 170–610°C temperature range and this loss in mass may be due to the exothermic but not endothermic continuous decomposition of the ligand as reported by Kanagaraj and Rao [5].

Before discussing the thermal behaviour of the metal complexes, it is essential to comment on the thermal behaviour of different types of water i.e. hygroscopic water, water of crystallization and chemically bound or coordinated water. The removal of hygroscopic water occurs in the 80–105°C region while 105–220°C for water of crystallization. The region of coordinated water lies in the range 220–550°C. However these ranges of temperature for the removal of water are not unique. Depending upon the magnitude of the interactions of different types of water molecules, these temperature ranges vary significantly from one system to another.

The characteristic parameters of TG, DTG and DTA curves of Ag(I)–SMZ complex are recorded in Table 1. The data of DTG and TG curves reveal that the decomposition of the complex occurs in two exothermic steps (Table 1). The first step of decomposition starts at 225°C. The broad character of the second DTG peak reveals that in decomposition of the complex, a number of reactions are involved with the formation of unstable intermediate species. The temperature range for the decomposition of complex in two steps is 225–610°C. The loss in mass is of the order of 67% (expected value 72%) which corresponds to the removal of one molecule of water as well as one molecule of SMZ, with the formation of Ag at 610°C. The mass of the Ag residue is of the order of 33% and is 5% above the expected value. Keeping in view the mass loss as a function of temperature, the scheme for the decomposition of the complex may be presented as:

$$[Ag(SMZ)H_2O] \xrightarrow[-\ SMZ]{-\ H_2O} Ag \qquad (1)$$

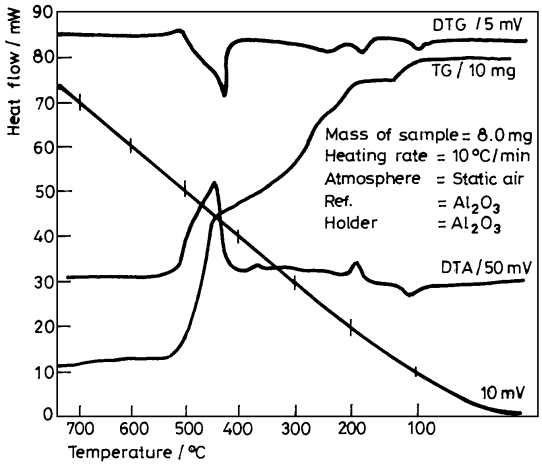

Fig. 4 TG, DTG and DTA curves of $[Co(SMZ)_2(H_2O)_2]\cdot H_2O$

The TG, DTG and DTA parameters of Cd(II)–SMZ complex indicate that decomposition occurs in three steps (Table 1). The first step in the temperature range 110–140°C is endothermic in nature and is assigned to the removal of two molecules of chemically bound water. The loss in mass corresponding to this step is 5.6%. The second and third exothermic steps fall in the temperature range 230–530°C. These steps correspond to the decomposition of $Cd(SMZ)_2$ to CdO. A 77.5% loss has been observed in this step as expected. CdO is the stable form up to 900°C. The residual mass due to CdO is ~16% which is well within the range of expected value i.e. 19.6%. In view of the above facts, decomposition of the complex may be written as:

$$[Cd(SMZ)_2(H_2O)_2] \xrightarrow[a]{-2H_2O} Cd(SMZ)_2 \xrightarrow[b]{-2SMZ} CdO \qquad (2)$$

The thermal decomposition of VO(II)–SMZ complex occurs in four stages as is evident from the characteristic parameters of TG, DTG and DTA curves (Table 1). The endothermic 4% loss in mass in the temperature region 40–70°C may be due to the removal of hygroscopic water. The second stage falls in the temperature region 110–200°C. The loss of coordinated water corresponding to this stage is of the order of 6% and is also endothermic in nature. The exothermic loss in mass in the temperature region 200–400 and 400–530°C is around 40 and 42% respectively which is well within the expected value. The loss in mass in two stages is attributed to the thermal removal of two ligand molecules with the formation of V_2O_5 at 530°C. The broad nature of DTG curve reveals that in these two steps a number of reactions are taking place simultaneously with the formation of unstable intermediate moities. The residual mass due to V_2O_5 is of the order of 13% and remains stable upto 690°C as expected. Keeping in view, to above discussion, the following scheme is proposed for the thermal decomposition of the complex:

$$[VO(SMZ)_2(H_2O)_2] \xrightarrow[a]{-2H_2O} VO(SMZ)_2 \xrightarrow[b]{-2SMZ} V_2O_5 \qquad (3)$$

The characteristic parameters of TG, DTG and DTA curves of UO_2(II)–SMZ complex show that thermal decomposition of the complex is a four step process. The first step is endothermic in character and is in the temperature range 25–50°C and is due to the hygroscopic water. The loss in mass corresponding to this step is 3%. The second step in the temperature range 50–150°C which is also endothermic represents the loss of one molecule of water of crystallization. The mass loss is of order of 2.4% and is well within the range of expected value. The third and the fourth steps which are exothermic in nature fall in the temperature range 105–620°C. The mass loss in this temperature range have been found to be of the order of 62%. This may be attributed to the decomposition of two SMZ molecules from the complex, finally with the formation of U_3O_8 via UO_3 at 620°C. The broad nature of DTG and DTA curves corresponding to the fourth step indicates that the number of reactions are taking place simultaneously without giving stable intermediate species. Beyond 620°C, there is no measurable change in the mass. In brief, the thermal changes can be shown as:

$$UO_2(SMZ)_2H_2O \xrightarrow[a]{-H_2O} UO_2(SMZ)_2 \xrightarrow[b]{-SMZ} UO_2(SMZ) \xrightarrow[c]{-SMZ} U_3O_8 \qquad (4)$$

The decomposition of Co(II)–SMZ complex takes place in four steps as is evident from the characteristic parameters of TG, DTG and DTA curves. The first endothermic step in the temperature region 100–130°C shows a 3% mass loss and is attributed to the one molecule of water of crystallisation. The 5.8% mass loss in the second endothermic step in the temperature region 185–240°C is due to two molecules of chemically bound water. The third and fourth steps are exothermic in nature and fall in the temperature range 240–450 and 450–535°C respectively. The observed mass loss corresponding to these steps is of the order of 40% in each step. This mass loss corresponds to the thermal removal of two ligand molecules from the complex consequently with the formation of stable Co_3O_4 at 535°C. In the light of above discussion, the decomposition of the complex may be presented as:

$$\begin{gathered}[Co(SMZ)_2(H_2O)_2]\cdot H_2O \xrightarrow[a]{-H_2O} [Co(SMZ)_2(H_2O)_2] \xrightarrow[b]{-2H_2O} \\ [Co(SMZ)_2] \xrightarrow[c]{-SMZ} [Co(SMZ)] \xrightarrow[d]{-SMZ} Co_3O_4\end{gathered} \qquad (5)$$

The characteristic parameters of TG, DTG and DTA curves of Hg(II)–SMZ complex reveal that the thermal decomposition of Hg(II)–SMZ complex occurs in two steps in the temperature regions upto 180 and 180–600°C respectively. First step is endothermic and correspond to the loss of two coordinated water molecules with 4.8% loss in mass. The second decomposition temperature ranges from 180–600°C and is exothermic in character. The broad nature of DTA peak in this temperature range is indicative of the fact that number of chemical reactions are occurring simultaneously with the formation of unstable intermediate moities. The loss in mass during this step is of the order of 92% and this may be due to the thermal removal of two molecules of ligand, as well as the decomposition of HgO formed to Hg. In the light

Table 1 The characteristic parameters of TG, DTG and DTA curves of SMZ and its metal complexes

Compound	TG			DTG	DTA	Reaction, steps
	T_{range}/°C	Mass loss/%		Peaks/°C		
		obs.	calc.			
$C_{10}H_{11}N_3O_3S$	170–610	100	100	175b	180(exo) 465b(exo)	exothermic continuous decomposition
$[Ag(SMZ)H_2O]$	225–610	67.0	71.4	190	200(exo)	exothermic decomposition of the complex with the formation of Ag, (1)
	>610	33.0*	28.6	440b	435b(exo)	Ag
$[Cd(SMZ)_2(H_2O)_2]$	110–140	5.6	5.5	100	110(endo)	endothermic removal of two coordinated water molecules, (2)a
	230–530	77.5	81.7	250	250(exo)	exothermic removal of two SMZ molecules and formation of CdO, (2)b
	530–900	16.0*	19.6*	520	485(exo)	CdO
$[VO(SMZ)_2(H_2O)_2]$	40–74	4.0	–	45	55(endo)	endothermic removal of hygroscopic water
	110–200	6.0	6.1	170	110(endo)	removal of two molecules of coordinated water, (3)a
	200–400	40.0	90.8	215b	180(exo)	decomposition of two molecules of SMZ with the formation of V_2O_5, (3)b
	400–530	42.0		340b	390(exo)	V_2O_5
	530–690	13.0*	15.4*			

Table 1 Continued

Compound	TG			DTG	DTA	Reaction, steps
	T_{range}/°C	Mass loss/%		Peaks/°C		
		obs.	calc.			
$[UO_2(SMZ)_2]\cdot H_2O$	25–50	3.0	–	50	60(endo)	endothermic removal of hygroscopic water
	50–105	2.4	2.2	90	115(endo)	removal of one molecule of water of crystallization, (4)a
	105–620	62	65.1	180	185(exo)	decomposition of two molecules of SMZ with the formation of U_3O_8,via UO_3 (3)b,c
	>620	35.0*	35.4*	485b	485(exo)	U_3O_8
$[Co(SMZ)_2(H_2O)_2]\cdot H_2O$	100–130	3.0	2.9	100	110(endo)	endothermic removal of one molecule of water, (5)a
	185–240	5.8	6.0	180	200(exo)	endothermic removal of two molecules of coordinated water, (5)b
	240–450	40.0	89.4	240	450(exo)	removal of two molecules of SMZ with the formation of Co_3O_4 at 535°C, (5)c,d
	450–535	40.0				
	>535	12.0*	13.0*	430		Co_3O_4
$[Hg(SMZ)_2(H_2O)_2]$	upto 180	4.8	4.9	180	130(endo)	endothermic removal of two coordinated water molecules, (6)a
	180–600	92.0	95.1	460b	460(exo)	exothermic removal of two molecules of SMZ, (6)b,c along with the decomposition of HgO formed to Hg, (6)d

*- residual mass, b - broad

of this discussion, the scheme for the thermal decomposition of Hg(II)–SMZ complex may be presented as:

$$[Hg(SMZ)_2(H_2O)_2] \xrightarrow[a]{-2H_2O} [Hg(SMZ)_2] \xrightarrow[b]{-SMZ}$$
$$[Hg(SMZ)] \xrightarrow[c]{-SMZ} HgO \xrightarrow[d]{} Hg \qquad (6)$$

To summarise, it is concluded that in these complexes, the mass loss as a function of temperature occurs as expected from the molecular formula as deduced from elemental analysis.

* * *

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References

1 K. Florey (Ed.), 'Analytical profiles of drug substances', Vol 3, Academic Press New York, (1973) 469.
2 S. Kirschner, Y. K. Wei, D. Francis and J. G. Bergman, J. Med. Chem., 9 (1966) 369.
3 A. J. Thomson, R. J. P. Williams and S. Reslova, Structure and Bonding, 11 (1972) 1.
4 B. S. Sekhon, H. K. Sahai and H. S. Randhawa, J. Biol. Inorg. Chem., (Communicated).
5 G. Kanagaraj and J. N. Rao, Synth. React. Inorg. Met. Org. Chem., 22 (1992) 559.